(19) FEDERAL REPUBLIC OF GERMANY
(12) GERMAN PATENT OFFICE
(11) PATENT NO: 3,306,528 A1 (Offenlegungsschrift)

(51) Int. Cl.^{3}: D 21 H 3/78; D 21 H 5/00; D 21 H 5/18
(21) Application No: P 33 06 528.4
(22) Filing Date: February 24, 1983
(43) Laid-Open to Public Inspection: July 5, 1984

(30) Priority Data
(32) Date: December 30, 1982
(33) Country: Germany
(31) Code: 32486677
(30) Priority Data
(32) Date: April 3, 1982
(33) Country: Germany
(31) Code: 32125097
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Examination request filed according to Section 44, Patent Law.

(54) PAPER-, CARTON-, AND CARDBOARD-LIKE MATERIAL

A paper-, carton-, or cardboard-like material, produced from an aqueous, fibrous material suspension, containing a calcium hydrosilicate with a high residual moisture as a filler, which is preferably used crystallized in the shape of needles; it has a xonotlite structure and is produced in a hydrothermal process with various hydration stages. The calcium hydrosilicate has the special capacity of binding hydrogen bridges. It can thus be bound advantageously into the hydrogen bridges between the fibers to support the structural strength of the sheet formation of the material, and may also bind the hydrogen bridges among one another. Inorganic fibers can also be used, exclusively or predominantly, so as to obtain noncombustible or not easily flammable papers, cartons, and cardboards. Preferably, then, a synthetic magnesium-aluminum silicate fiber in

combination with glass fibers is used. The inorganic fibers are coated and activated on the surface, at least in parts, by means of an organic polyelectrolyte, so as to activate them to form hydrogen bridge bonds.

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PATENT CLAIMS

1. Paper-, carton-, or cardboard-like material, produced by the formation of sheets from an aqueous, fibrous material suspension and the dehydration of the material suspension on a screen with a subsequent drying, wherein the structural strength of a sheet is dependent on hydrogen bridges, which form between the individual fibers during the dehydration, characterized in that crystalline calcium silicate with various hydration stages is provided as the filler with a hydrogen-bridge binding capacity, which is bound into the hydrogen bridges between the fibers to support the structural strength of the sheet.

2. Material according to Claim 1, characterized in that the crystallized calcium hydrosilicate has a high length-width ratio and a width dimension below 1 µm.

3. Material according to Claim 2, characterized in that the crystallized calcium hydrosilicate has a length-width ratio of 10:1 to 200:1.

4. Material according to Claims 2 and 3, characterized in that the crystallized calcium hydrosilicate has a xonotlite structure.

5. Material according to Claims 2 and 3, characterized in that the calcium hydrosilicate is a hydrated wollastonite.

6. Material according to Claim 4 or 5, characterized in that the xonotlite, crystallized in the form of needles, or calcium hydrosilicate, crystallized in the shape of strips, has a length/width ratio of 100:1 to 50:1 and width dimensions below 1 µm.

7. Material according to one of Claims 1 to 6, characterized in that the calcium hydrosilicate is produced synthetically in the hydrothermal process and essentially has the formula $6CaO \cdot 6SiO_2 \cdot nH_2O$ or $Ca_6[(OH)_2Si_6O_{17}] \cdot nH_2O$, wherein the residual moisture is 2 to approximately 50 wt% H_2O, preferably 35 to 50 wt% H_2O.

8. Material according to Claim 1, characterized in that the fibers consist, at least partially, of synthetic magnesium-aluminum silicate fibers, produced in the hydrothermal process.

9. Material according to Claim 8, characterized in that the magnesium-aluminum silicate fibers consist, on average, of approximately 45% SiO_2, 20% CaO, 15% MgO, 12% Al_2O_3, 3% NaO, and 5% Fe.

10. Material according to Claim 8 or 9, characterized in that the magnesium-aluminum silicate fibers have a length of 1 to 5 mm with an average diameter of 3 to 5 µm.

11. Material according to Claim 4, characterized in that a fraction of the inorganic fibers consists of glass fibers.

12. Material according to Claim 7, characterized in that the glass fibers have a length of 3 to 12 mm, preferably 3 to 6 mm, and an average diameter of 10 to 14 μm, preferably 12 to 13 μm.

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Paper-, carton-, or cardboard-like material

The invention concerns a paper-, carton-, or cardboard-like material, produced by the formation of sheets from an aqueous, fibrous material suspension and the dehydration of the material suspension on a screen with a subsequent drying, wherein the structural strength of a sheet is dependent on hydrogen bridges, which are formed between the individual fibers during the dehydration.

The importance of inorganic fillers with regard to certain paper, carton, and cardboard qualities, such as the degree of whiteness, smoothness, opacity, and imprintability, are known.

The structural resistance of paper-, carton, or cardboard-like materials is, as is known, dependent on the number of hydrogen bridges between the fibrous carrier materials of the material, which form during the dehydration of the material suspension. The structural strength of the material is, however, reduced with an increasing filler content, since the traditional inorganic fillers block or prevent the formation of hydrogen bridges between the fibers.

With traditional, readily combustible paper-, carton, and cardboard-like materials with cellulose fibers as the carrier material, hydrogen bridges are formed between hydroxyl groups on the surface of the cellulose fibers. No hydrogen bridges are formed, on the other hand, between inorganic fibers. Therefore, rigidity and/or crosslinking auxiliaries (organic polyelectrolytes) are needed, which deposit adsorptively, at least in places on the inorganic fiber surfaces, in order to form coated, activated fiber sites, between which hydrogen bridges are formed during the dehydration of the material suspension for the binding of the inorganic fibers, comparable to cellulose fibers.

The goal of the invention is to produce a paper-, carton-, or cardboard-like material whose quality can be adjusted by a filler, which neither blocks nor hinders the structural strength of the sheet-shaped material because of its special characteristics, but in contrast to the known fillers, supports or positively influences the structural strength.

The goal is attained in that, in accordance with the invention, crystalline calcium silicate with various hydration stages, which is bound into the hydrogen bridges between the fibers to

support the structural strength of the sheet, is provided as the filler having a hydrogen bridge binding capacity.

Advantageous embodiments can be deduced from the features of the subclaims.

The filler, in accordance with the invention, thus has a special affinity for organic fibers and for coated, activated inorganic fibers with a hydrogen bridge binding capacity, and thus differs substantially from traditional fillers, such as talc, kaolin, gypsum, heavy spar, chalk, magnesite, dolomite, titanium white, zinc spar, and zinc white.

It is particularly advantageous if a calcium hydrosilicate, crystallized into the shape of needles, and with a xonotlite structure, is used. Such calcium hydrosilicates can be advantageously produced synthetically in the hydrothermal process and essentially have the formula $6CaO \cdot 6SiO_2 \cdot H_2O$ or $Ca_6[(OH)_2Si_6O_{17}] \cdot nH_2O$. Thus, calcium hydrosilicate, as is known, can be produced by a direct synthesis of lime and silicic acid, under certain mineralization conditions, by precipitation processes, or from lime and quartz sand with water, under pressure at high temperatures, wherein the quantitative ratios can be varied according to the desired end product and thereby several hydration stages can be aimed at, in order to be able to ensure residual moistures of 2 to approximately 50 wt%. Different residual moistures of the crystalline synthetic calcium hydrosilicates are obtained during production by various hydration stages.

Surprisingly, it was shown that a xonotlite with a minimum residual moisture, and approximately in accordance with the formula $6CaO \cdot 6SiO_2 \cdot H_2O$ or $CaO \cdot SiO_2 \cdot 0.2H_2O$, does not have a hydrogen bridge binding capacity. Apparently, this is related to the fact that siloxane groups are extensively present on the surface of the xonotlite crystals, and only isolated silanol groups are present. However, the greater the water content of the synthetic xonotlite, the greater the fraction of the silanol groups that can be formed on the xonotlite crystal surface and that are able to bind hydrogen bridges.

The inventor therefore recognized, in particular, that such synthetic, crystalline calcium silicates of various hydration stages can be well used as fillers with a hydrogen bridge binding capacity in the sense of the goal of the invention, and which have a relatively high residual moisture, preferably 2 wt% to approximately 50 wt% H_2O and more, preferably around 40 to 50 wt% H_2O.

Xonotlite calcium hydrosilicates have a high specific surface [area] and contain less than 1% free crystalline silicic acid.

Also, under defined drying conditions, crystalline calcium hydrosilicates with residual moistures of 2 wt% to approximately 50 wt% can be formed. By means of differential thermoanalysis and differential thermogravimetry, changes in the xonotlite calcium hydrosilicate are revealed in the temperature range above 500°C, which can be clarified by conversion of the xonotlite structure to the wollastonite structure.

Synthetic, crystalline calcium hydrosilicates with high residue moistures have a short ageing capacity with access to air. This apparently is related to the fact that with the access to CO_2 in the air to the surfaces of the water-rich calcium hydrosilicates, carbonates are formed; they thwart the hydrogen bridge binding capacity, and therefore apparently block the silanol groups present. It became evident that a xonotlite with a residual moisture of approximately 42% H_2O had substantially lost its good hydrogen bridge binding capacity with a storage time of 1 week. Aside from the surface carbonization, this may also be related to the fact that with a longer storage of synthetic crystalline calcium hydrosilicate with a high water content, water is secreted. It is important thereby that these are original water contents. Xonotlite with low water contents, and which has no hydrogen bridge binding capacity, does not allow this in that one prepares it under turbid aqueous conditions and carries out stirring for a longer period of time.

The advantageous characteristics of the filler in accordance with the invention are also effective if the fibers at least partially consist of synthetic magnesium-aluminum silicate fibers, produced in the hydrothermal process. Such silicate fibers consist, on the average, of 45% SiO_2, 20% CaO, 15% MgO, 12% Al_2O_3, 3% NaO, and 5% Fe, and can have a length of 1 to 5 mm with an average diameter of 3 to 5 µm. A known method for the production of such silicate fibers is disclosed in West German Patent No. 2,829,692 (Offenlegungsschrift).

The inorganic fibers can advantageously contain glass fibers as well. The glass fibers can have a length of 3 to 12 mm and an average diameter of 10 to 14 µm. Preferably, the glass fibers have a greater length than the magnesium-aluminum silicate fibers, produced in the hydrothermal process.

So that the inorganic fibers are able to bind hydrogen bridges, they are coated and activated, at least in parts, by the addition of rigidity and/or crosslinking auxiliaries in the form of organic polyelectrolytes.

According to the invention, above all, noncombustible or not readily flammable papers, cartons, and cardboards can be indicated or produced in this way, consisting exclusively or predominantly of inorganic fibers and at least one organic filler having a remarkable affinity for the activated, coated inorganic fibers and which can be advantageously bound into the hydrogen bridges between the activated inorganic fibers due to its capacity to bind hydrogen bridges; it also binds hydrogen bridges among themselves so as to, in this way, support or at least positively influence the structural strength between the fibers, the fibers and the fillers, and between the fillers.

Fire Resistance Classes F30, F60, and F90 of Construction Materials of Class A1 and Class A2 are defined according to the German Industrial Norm DIN 4102 "Burning behavior of construction materials and construction parts," September 1977 issue. The invention thus comprises, above all, noncombustible or not readily flammable papers, cartons, and cardboards, which fulfill at least the F30 condition for construction materials of Class A1 and Class A2. The

papers, cartons, and cardboards, in accordance with the invention, can be made so that they can have seams and grooves, and so that they are suitable for the production of fireproof packagings such as cartons and boxes. The materials can be imprinted by means of any known method. By a corresponding surface treatment, the papers, cartons, and cardboards, in accordance with the invention, have practically no limits with regard to their usability, above all, in the construction sector, including the construction of studios and exhibitions, as well as for displays. The papers, cartons, and cardboards, in accordance with the invention, can be made of inorganic fibers or predominantly of fibers that are advantageously free of asbestos fibers.

Due to the high residual moisture contents of the calcium hydrosilicate fillers used, in accordance with the invention, in noncombustible or not readily flammable papers, cartons, and cardboards, such paper or cardboard materials advantageously have a surprisingly high heat insulation capacity when they are exposed to extremely high temperatures, such as in fires. This is apparently related to the fact that the fillers in accordance with the invention have such a high heat insulation capacity until they have released their bound water under the effect of high temperatures and have apparently more or less been converted from a xonotlite structure into a wollastonite structure.

In accordance with the invention, it is possible to attain particularly good results if the crystallized calcium hydrosilicate has a length/width ratio of 10:1 to 200:1, when the crystallized hydrosilicate has, moreover, a xonotlite structure or is a hydrated wollastonite. The xonotlite, which is crystallized in the shape of needles, or the calcium hydrosilicate, which is crystallized in the shape of strips, advantageously also has a length/width ratio of 100:1 to 50:1 and has width dimensions below 1 μm.

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TRANSLATIONS

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German Patent No: 3,306,528 A1

Translated from German into English
by Phoenix Translations Code No. 65-3513

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